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Thermally Emitting Iron Aerogel Composites

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Aerogels are a class of materials with extremely high surface area and porosity. An exothermic reaction that takes place on the hundreds of square meters/gram of aerogel surface area could result in substantial thermal emission. Here we report various air-sensitive, thermally emitting aerogels based on the exothermic reaction of iron metal to iron oxide. Aerogels containing iron, either as a component of the nanoscale aerogel structure or as a vapor-deposited coating on an aerogel substrate have been prepared and evaluated. Using the first approach, composite aerogels of iron and silica have been produced via a solution-gelation (sol-gel) route, however none of these materials produced any detectable heat when exposed to air. Using the second approach, iron was deposited on silica, carbon and resorcinol/formaldehyde (RF) aerogels by metal organic chemical vapor deposition using ferrocene and iron pentacarbonyl as iron precursors. While the silica aerogels coated with iron from iron pentacarbonyl emitted low, but detectable, amounts of heat, the most energetic materials were carbon and RF aerogels deposited with iron from iron pentacarbonyl. Oxidation of the deposited iron on both carbon and RF aerogels created enough heat to ignite the aerogel substrates. These samples burned at ~600 to 700 °C for a duration that depended on sample size. The iron/carbon composites burn relatively cleanly, however combustion of the RF substrate results in the release of volatile organic compounds including benzene and toluene. ...

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EXECUTIVE SUMMARY

Aerogels are a class of materials with extremely high surface area and porosity. An exothermic reaction that takes place on the hundreds of square meters/gram of aerogel surface area could result in substantial thermal emission. Here we report various air-sensitive, thermally emitting aerogels based on the exothermic reaction of iron metal to iron oxide. Aerogels containing iron, either as a component of the nanoscale aerogel structure or as a vapor-deposited coating on an aerogel substrate have been prepared and evaluated. Using the first approach, composite aerogels of iron and silica have been produced via a solution-gelation (sol-gel) route, however none of these materials produced any detectable heat when exposed to air. Using the second approach, iron was deposited on silica, carbon and resorcinol/formaldehyde (RF) aerogels by metal organic chemical vapor deposition using ferrocene and iron pentacarbonyl as iron precursors. While the silica aerogels coated with iron from iron pentacarbonyl emitted low, but detectable, amounts of heat, the most energetic materials were carbon and RF aerogels deposited with iron from iron pentacarbonyl. Oxidation of the deposited iron on both carbon and RF aerogels created enough heat to ignite the aerogel substrates. These samples burned at ~600 to 700 °C for a duration that depended on sample size. The iron/carbon composites burn relatively cleanly, however combustion of the RF substrate results in the release of volatile organic compounds including benzene and toluene.

THERMALLY EMITTING IRON AEROGEL COMPOSITES

INTRODUCTION

One mechanism for generating heat is the exothermic oxidation of various metals, including iron, nickel, aluminum and bismuth. By preparing the metal as a fine powder, the surface area is increased and the amount of heat generated on a volume basis also rises. In addition, the finely divided metal particles spontaneously emit heat upon exposure to oxygen or air, thereby avoiding the need for other sources of ignition. For some applications, it is desirable to have bulk, or monolithic, material, rather than a powder, such as flammable fuels. Metals, such as iron, nickel, or cobalt, can be modified by a diffusion and leaching process that yields a highly porous surface layer, thereby increasing the area of metal surface available for oxidation and hence the amount of heat generated [1–3]. Because these processes are based on diffusion through solids, the modified layer is typically thin and only when prepared as a foil can a significant fraction of the bulk be made porous.

Aerogels are a class of nanostructured materials with unique properties that make them candidates for a new, bulk thermal emitter. Typically, aerogels are prepared by synthesizing a gel using a solution-gelation (sol-gel) process, followed by the removal of the solvent phase under supercritical conditions, thereby avoiding the formation of large capillary forces that cause shrinkage during drying. This process preserves the very porous, open network of the gel, and leads to extreme physical properties. Based on small-angle scattering and transmission electron microscopy (TEM), the structure of aerogels typically consists of ~10-nm particles connected in an open network [4–8]. Aerogels contain both microporosity (<2 nm pores) within the particles and mesoporosity (2 to 50 nm pores) between the particles, which results in both very high surface area and good permeability. For example, silica aerogels have been prepared with porosities of >99%, densities as low as 0.002 g/cm^3, and surface areas of up to 1000 m^2/g [9].

Two approaches have been considered in an effort to take advantage of aerogel properties for thermal emitters. The first approach was to synthesize an aerogel that had finely divided iron as part of its nanoscale structure. The second approach was to infiltrate known aerogel substrates with an iron coating. The deposition of iron on silica aerogel substrates has been reported previously by Arlon Hunt and co-workers at Lawrence Berkeley Laboratory [10–13]. They observed pyrophoric behavior upon exposure to air after deposition of either ferrocene or iron pentacarbonyl on silica aerogel. We have sought to optimize the thermal signature and lifetime of this pyrophoric response by modifying the substrate composition and the deposition parameters.

EXPERIMENTAL PROCEDURE

Aerogel Preparation

Silica Aerogel

Acid-catalyzed silica aerogels were prepared via a sol-gel method similar to that described elsewhere [14 and references therein]. A solution of tetramethoxysilane (TMOS), water and 0.04 N HCl was prepared with a ratio of 1 : 0.222 : 0.0138 by weight. (A single batch was made using 2.545 g of TMOS, but double and triple batches have been prepared as well.) This solution was ultrasonicated for 10 min. A

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potassium hydrogen phthalate (KHP) buffer solution with pH = 4.6 was added, while stirring, to the TMOS solution such that the TMOS:buffer ratio was 2:3 or 2:4 by volume, and then immediately poured into 5-ml polyethylene molds. The samples gelled in 3 to 5 min. The gels were allowed to age for one to four days. They were then removed from the molds, placed in acetone and washed daily for four to five days. The acetone-filled gels were placed in a critical-point dryer, flushed several times with liquid CO_2, and then dried by releasing the CO_2 under supercritical conditions. Residual organics and adsorbed water were removed from the dried aerogels by heating at 2 °C/min in air to 500 °C and holding for 30 min before cooling.

Fe-Si Oxide Aerogels

A modified version of the silica gel preparation described above was developed for preparation of Fe-Si oxide aerogels. Iron chloride hydrate ($FeCl_2 \cdot yH_20$) was hydrolyzed by NaOH in a buffer solution to form $Fe(OH)_x$ in solution, which then condensed with the silica to form the $FeOx/SiO_2$ aerogel. The (Fe+Si):water ratio was fixed at 1:20, and the Fe:Si ratio at 4:1.

KHP buffer (pH = 4.6) and NaOH were combined, the iron salt was added and the mixture was stirred for about 30 min. The pH was adjusted to about 5.5 with the drop-wise addition of concentrated HCl. The TMOS + H_2O + HCl solution, prepared as described for the silica aerogel synthesis, was stirred into the iron solution. In initial mixtures, the pH was observed to increase with time; gelation, if it occurred at all, was reversed. In order to maintain an acidic environment, up to 120 drops of concentrated HCl was added to t the Fe-Si solution before it was poured into 5-ml polyethylene molds. The samples gelled within 3 min and were aged in the molds for at least four days. [1] The gels were removed from the molds and transferred to a glass vial in which they were washed at least daily in water for two days to remove the chloride, then in acetone for two more days. They were dried, as describe above, under supercritical CO_2.

The dried gels were reduced in a flowing mixture of 315 ccm (cm^3/min) argon /35 ccm hydrogen (10%) or 180 ccm argon/35 ccm hydrogen (16%) at 500 °C for at least 3 h.

Resorcinol/Formaldehyde Aerogel

Two types of resorcinol/formaldehyde (RF) aerogel were used. One type was prepared by the method developed by Pekala [15–17] in which a gel is formed by base-catalyzed aqueous polycondensation of a resorcinol-formaldehyde mixture. The gel is then aged, washed, and supercritically dried in a manner similar to that used to prepare the silica aerogels. RF aerogels prepared by this method were provided by Aerojet Corporation and are referred to as "Aerojet RF" aerogels.

The second type of RF aerogel was obtained from Ocellus Corporation. Although chemically similar, the company has developed a proprietary process in which certain parameters are modified during the sol-gel reaction. The resulting gel structure is strengthened such that it can be dried under ambient conditions without significant collapse or shrinkage of the pores. These materials are referred to as "Ocellus RF" aerogels.

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[1] Solutions prepared by this route using $FeCl_3 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ as the iron source did not gel.

Carbon Aerogel

Pure carbon aerogel was formed by the pyrolysis of RF aerogel, following the procedure described by Pekala and Alviso [18]. RF aerogel samples were heated under flowing Ar at 2 °C/min to 250 °C, held for 4 h, heated at 1.4 °C/min to 1050 °C, held for another 4 h and then cooled at ~2 °C/min by turning off the power to the furnace. Aerojet RF aerogels pyrolyzed by this procedure are referred to as "Aerojet carbon" aerogels. "Ocellus carbon" aerogels were prepared by the manufacturer using a similar procedure and were used as-received.

Metal Organic Chemical Vapor Deposition (MOCVD)

The material deposited by MOCVD depends on many factors, including metal precursor compound, substrate composition and various depositional parameters. Two different iron metal precursors (ferrocene and iron pentacarbonyl) were used to deposit elemental iron onto the surface area of various aerogel substrates. In order to minimize possible reaction with adsorbed species on the aerogel surface, the substrates were heated to 180 to 250 °C immediately prior to deposition, if the reactor configuration permitted.

Ferrocene Deposition

Ferrocene (C_5H_5Fe), which is a solid at room temperature, was used as a precursor for deposition only on silica aerogels. Two flowthrough setups and two sealed methods were investigated. Figure 1 shows the two flowthrough setups. In the first (Fig. 1(a)), the ferrocene and aerogel were in separate glass tubes (12-mm OD/10-mm ID), connected by 6-mm Teflon tubing. The glass tube containing the ferrocene and the Teflon tubing were heated to ≥100 °C using heat-tape. The separation of the ferrocene and substrate allows them to be heated independently, permitting removal of adsorbed water prior to deposition and allowing the sample and precursor to be held at different temperatures during deposition. The carrier gas was argon flowing at a rate of 100 ccm. Typically, the ferrocene temperature was ≥100 °C, the substrate temperature was 400 °C, and the deposition time was between 20 and 24 h.

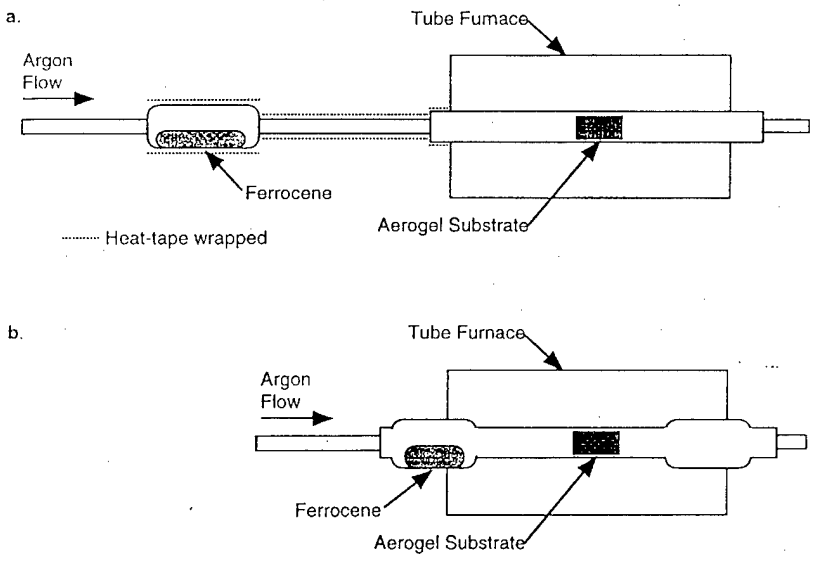

Fig. 1. Flowthrough setups used for ferrocene deposition. (a) Separate precursor and substrate tubes. (b) Precursor and substrate in single, custom-made tube.

Several runs in the first flowthrough setup failed when cold spots occurred along the heated path between the precursor and the substrate, causing ferrocene to deposit and clog the tube. In order to avoid this problem, a second flowthrough setup was designed, in which the ferrocene and the substrate were placed in a custom-made glass tube with two bulges, shown in Fig. 1(b). The bulge "upstream" from the substrate acts as a reservoir for the ferrocene precursor, and the bulge "downstream" acts as a trap for excess volatilized ferrocene thereby preventing clogs. The tube was initially positioned so that the ferrocene was outside the heated zone, which allows the substrate to be preheated while the ferrocene remains below its sublimation temperature. When the substrate reached the deposition temperature, the tube was repositioned in the furnace so that the ferrocene was heated above 100 °C and, thereby, volatilized. In this setup, the substrate temperature was 400 °C, and the carrier gas was argon flowing at 100 ccm.

Two sealed, or static, setups were also used. In the first, ferrocene and silica aerogel were placed in a sealed Pyrex glass ampoule, evacuated prior to sealing using a standard roughing pump. The sealed ampoule was heated to 400 °C and held for 20 to 24 h. One drawback to this technique was frequent cracking of the ampoules during deposition.

In the second sealed setup, the aerogel and ferrocene were placed in an evacuated, sealed steel "bomb". The bomb was easier to load than the glass ampoule and less likely to fail, however Teflon components in the valve limited the deposition temperature to <200 °C. After loading, the bomb was heated to a temperature below the melting point of ferrocene (173 °C), generally between 150 °C and 170 °C, and held for 24 to 48 h. After unloading, the sample was heated at 500 °C for 3 h in flowing argon/hydrogen to decompose the ferrocene to iron metal.

Iron Pentacarbonyl Deposition

Figure 2 shows the setup used for iron pentacarbonyl ($Fe(CO)_5$) deposition, which is a liquid at room temperature. By controlling three valves, the apparatus allows the carrier gas to either bubble through the liquid precursor before flowing into the sample tube or bypass the precursor and flow directly to the sample. Because iron pentacarbonyl is photosensitive, the apparatus was wrapped in foil. The carrier gas used was 65 ccm Ar and 3.2 ccm H_2 (5%); the small amount of hydrogen aided in maintaining the iron in a reduced state. In order to remove surface water, the aerogel substrate was heated under flowing Ar/H_2 at 5 °C/min to 250 °C, held 30 minutes, and cooled at 5 °C/min to the deposition temperature (between 90 °C and 150 °C). The valves on the bubbler were opened and the carrier gas allowed to bubble through the $Fe(CO)_5$ for 3 to 5 h. Following deposition, the bubbler was bypassed and pure carrier gas flowed through the sample tube as the temperature was decreased at 5 °C/min to room temperature. Some samples were subsequently heated to 400 °C for 1 hour under Ar/H_2 to further reduce the deposit to metal and to remove any remaining volatile organic compounds.

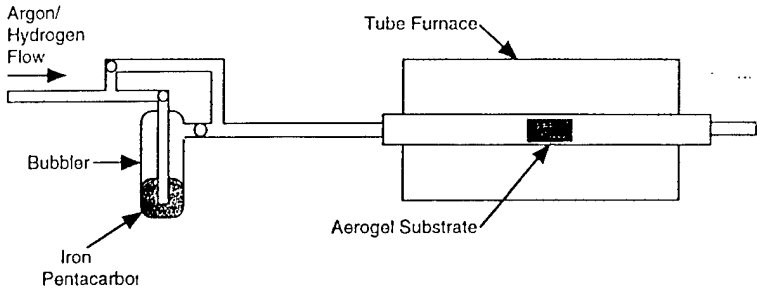

Fig. 2. MOCVD setup for iron pentacarbonyl deposition.

Aerogel Characterization

The presence and identification of crystalline phases were determined by powder X-ray diffraction (XRD) (Scintag XDS2000). In addition, crystallite size was calculated using the Scherrer equation,

$$\text{Crystal Size} = (0.9 * \lambda)/(\cos\theta * \text{FWHM}),$$

in which λ is the x-ray wavelength (Cu Kα = 1.54 Å), θ is the incident angle, and FWHM is the full width at half maximum in radians, corrected for the unbroadened peakwidth.

Surface area was determined by nitrogen gas adsorption using multipoint (Micromeritics ASAP 2010) and singlepoint (Quantachrome Monosorb) Brunauer, Emmett, and Teller (BET) techniques. Bulk density measurements were made by Archimedes' method in mercury, and skeletal density was determined by helium pycnometry (Micromeritics Accupyc 1330). Thermal gravimetric analysis (TGA) (TA Instruments 951 TGA or Rheometrics 1550 Simultaneous Thermal Analyzer) was carried out at a heating rate of 5 °C/min. A thin-wire, type-T thermocouple was used to measure the temperature of the sample surface during exposure to air. (Note that the true temperature may be a factor of two or more greater than the temperature measured by this method.)

The IR output of the air-reactive aerogel samples as a function of time was characterized in the laboratory by measuring the radiant intensity in the shortwave (SW), midwave (MW), and longwave (LW) IR bands. Each radiometer has a 20-degree field of view and contains a filter that is specific to one of the wavelength bandpasses. The radiant intensity in the SW band was measured using an Infrared Systems 12880 radiometer with a lead sulphide detector and noise equivalent irradiance (NEI) of 380 nW/cm^2. The intensity in the MW band was measured using a PRT-5 radiometer with a hyper-immersed thermistor bolometer detector and a NEI of 14 nW/cm^2. A second PRT-5 radiometer with a hyper-immersed thermistor bolometer detector and a NEI of 12 nW/cm^2 was used to measure the radiant intensity of the samples in the LW band. Each instrument was calibrated against a standard blackbody source (Barnes Model 11-210).

RESULTS

Fe-Si Oxide Aerogels

After the Fe and Si solutions were mixed and stirred for about 30 min, the mixture was a light green color and had a thick, pudding-like consistency. With the addition of a single drop of HCl, the color turned dark green and the consistency became much less viscous. Fe-Si solutions were made with pH varying from 12.7 to 5.1 by the addition of 0 to 120 drops of HCl, respectively. The more basic solutions, i.e. those prepared with 20 drops or less of HCl, did not gel. Solutions with pH between 5.1 and 5.8 (40 to 120 drops HCl added) gelled within 3 min. When samples were left exposed to air, the top layer of solution turned brown, and the pH steadily increased. This rise in pH is attributed to the oxidation reaction

$$4Fe^{2+} + 2H_2O + O_2 \rightarrow 4Fe^{3+} + 4OH^-.$$

Exposure to air was minimized in order to reduce this oxidation, thereby maintaining an acidic pH and encouraging gelation. During drying, the aerogels turned from green to brown. The dried samples were very weak monoliths, which strengthened during reduction due to sintering.

Based on XRD, iron metal was present in the Fe-Si oxide aerogels after a 3-h reduction in 5% hydrogen (315 ccm Ar/35 ccm H_2), along with residual NaCl (Fig. 3). The peak widths indicate an iron crystallite size of 54 nm. After 12 h of reduction, minor amounts of wustite (FeO) and fayalite (Fe_2SiO_4) are also present, in addition to iron metal and NaCl (Fig. 3).

None of the Fe-Si oxide aerogels made by the sol-gel route, and subsequently reduced, produced any detectable heat upon exposure to air.

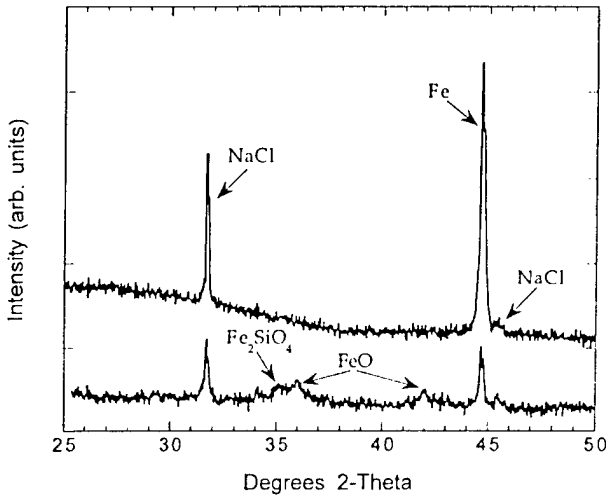

Fig. 3. XRD patterns for Fe-Si oxide aerogel reduced for 3 h (top) and 12 h (bottom).

MOCVD

The parameters and results for each MOCVD experiment are presented in the Appendix.

Substrate Characterization

Table 1 shows the properties of the aerogel substrates used in this study. The values are within the ranges typically reported for these materials, however several features are worth noting. While pyrolysis of RF to form carbon aerogel leads to as much as a 50 % reduction in volume, this loss is from both pore and skeletal volume. As a result the fractional pore volume changes little and the surface area, when expressed as area per unit volume, actually increases.

In spite of similar precursor chemistry, Ocellus RF and Aerojet RF materials have certain differences. The Ocellus material is orange whereas the Aerojet material is a very dark red. This difference is also observed in powdered samples, although the powdered Aerojet material is lighter in color than the monolith. The color difference between the Aerojet and Ocellus RF aerogels could be due to varying degrees of polymerization among the benzene rings.

The Ocellus and Aerojet carbon aerogels, derived by pyrolysis of RF aerogels, are also distinct. Based on high-resolution SEM images supplied by the company, the Ocellus carbon material is made up

of ~100-nm particles with pores that are 500 nm or larger. These dimensions, which have been confirmed by our group using small-angle neutron scattering, are almost an order of magnitude larger than the values reported for carbon aerogels prepared by the method used by Aerojet [16]. Presumably these differences between the carbon materials mimic parallel differences between the RF aerogels from which they are derived.

Table I Physical Properties of Various Aerogel Materials

Aerogel Material	Bulk Density (g/cm^3)	Skeletal Density (g/cm^3)	BET surface area (m^2/g [m^2/cm^3])	Pore Volume (%)	XRD results	Color / Appearance
Aerojet RF	0.244	1.55	415* [643]	84	amorphous	dark red / black
Aerojet Carbon	0.271	2.06 ‡	480† [989]	87	amorphous	black
Ocellus RF	0.272	1.44	na	81	amorphous	yellow / brown
Ocellus Carbon	0.303	2.04	350* [714]	85	amorphous	black
Silica	0.300	2.20#	650† [1430]	86	amorphous	translucent

* Measurement made using multi-point BET (Micromeretics ASAP 2010).

† Measurement made using single-point BET (Quantachrome Monosorb).

na - Measured values not available.

‡ From Ref. 1

Based on SANS measurements

Figure 4 shows TGA of silica (previously heated to 500 °C), Aerojet RF and Aerojet carbon aerogel substrates. Silica has ~5 wt % and carbon ~2 wt % adsorbed surface water, based on weight loss at ≤100 °C. The previously unheated RF aerogel loses weight continuously during heating to 500 °C due to removal of water and volatile organic species. TGA results for Ocellus RF and carbon were similar to the Aerojet RF and carbon curves, respectively. Since substrates were not reweighed after preheating prior to deposition, variation in the precise amounts of adsorbed water and organics precludes precise determination of weight gain during MOCVD.

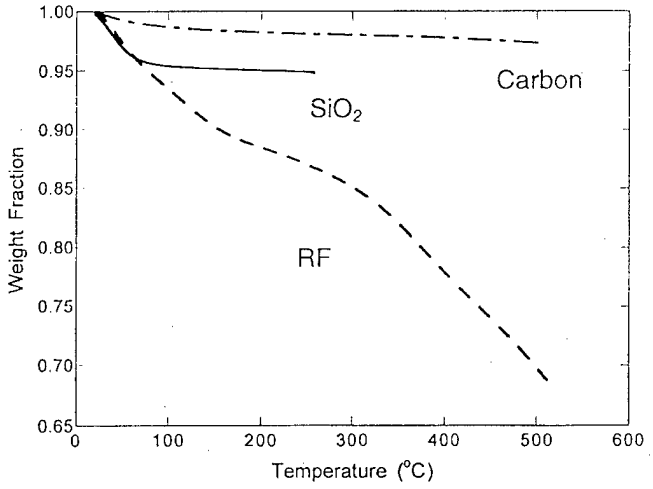

Fig. 4. TGA of aerogel substrates. The SiO_2 aerogel was heated previously to 500 °C, the RF aerogel was unheated, and the carbon aerogel was pyrolyzed at 1015 °C.

Ferrocene-Deposited Aerogels

The samples prepared using the first flowthrough setup (Fig. 1(a)) to deposit iron from ferrocene on silica aerogels had a metallic black rind and a translucent center, suggesting little penetration of the vapor phase into the aerogel interior prior to deposition. XRD indicates that the samples were mostly amorphous with a small amount of magnetite (Fe_3O_4). This setup was abandoned after a few runs due to frequent clogging of the tube connecting the ferrocene and sample tubes.

The ferrocene-coated silica aerogels prepared using the second flowthrough setup (Fig 1(b)) with a deposition temperature of 400 °C were uniformly black. When exposed to air, these samples radiated small amounts of heat. Although temperatures were not measured quantitatively, the samples reached approximately body temperature and stayed at that temperature for over one minute. The samples were completely amorphous.

Deposition in the sealed "bomb" at 150 to 170 °C produced samples that were uniformly colored throughout and that contain ferrocene as the only non-crystalline phase (based on XRD). After reducing the samples at 500 °C for 3 h, the ferrocene was completely decomposed (and presumably reduced). These samples, however, did not give off any noticeable heat when exposed to air. Exposed samples were completely amorphous.

In an effort to increase deposition and penetration of ferrocene in the silica aerogel, one sample was heated to 250 °C (above the boiling point of ferrocene) while still in the bomb after deposition at 150 °C.[2] Upon exposure to air, no detectable heat was given off. XRD analysis of this material showed predominantly ferrocene, along with a small amount of magnetite (Fig. 5). After reduction at 500° C for 3 h the sample still was not pyrophoric, and the XRD pattern showed an amorphous structure (Fig. 5).

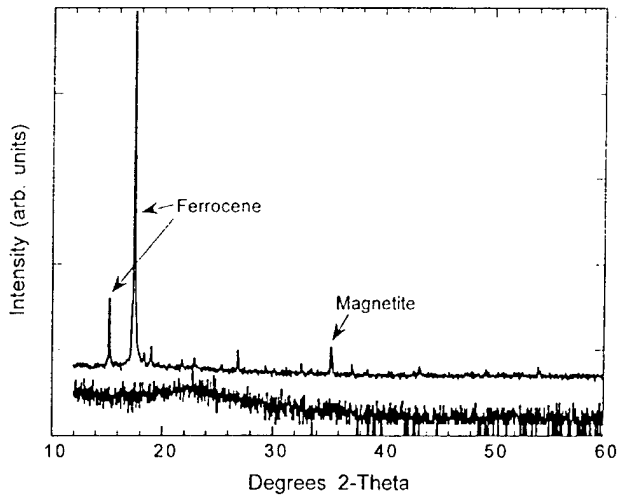

Fig. 5. XRD patterns of ferrocene-coated samples (48 hr at 150 °C plus 2 hr at 250 °C). Unannealed (top) and annealed/reduced in Ar/H_2 for 3 hr at 500 °C (bottom).

[2] The bomb valve was kept below 150 °C while the other end of the apparatus, which contained the sample, was heated to 250 °C.

Single-point BET measurements on the ferrocene-deposited sample from the second flowthrough setup showed a decrease in surface area from 654 m^2/g for the uncoated aerogel to 355 m^2/g for the coated sample.

Iron Pentacarbonyl-Deposited Aerogels

When the volatilized iron pentacarbonyl enters the heated sample tube, it is decomposed to iron metal, along with CO_2 and CO gas. The iron metal deposits on silica surfaces, including the walls of the sample tube. The degree to which the iron penetrates the aerogel substrate depends in part on the deposition temperature and gas flowrate.

Deposition on Silica Aerogel.

Silica aerogels deposited with decomposed iron pentacarbonyl had a gradient in color, from black near the outer edge to white or translucent (i.e. pristine substrates) in the center. At higher deposition temperatures (125 to 150 °C), the iron did not penetrate at all, forming a black rind on the outer surface of the aerogel. Upon exposure to air, most of these samples emitted enough heat to reach body temperature.

Increased penetration of the iron into the interior pores, as indicated by a black color throughout the sample, did not necessarily produce more heat. For instance, the sample deposited at 150 °C produced more heat than those deposited at 125 °C and 110 °C, though the degree of coverage appeared greater at the lower deposition temperatures. The maximum temperature achieved was strongly affected by post-deposition heat treatment. Samples heated at 400 °C for 1 h under flowing Ar/ H_2 reached up to 72 °C, and stayed above body temperature for over 1 min, whereas without this post-treatment, samples reached temperatures <50 °C.

The flow rate of the carrier gas also affected the iron penetration significantly. During most depositions, Ar/H_2 was flowing at 65 ccm/3.2 ccm in a tube with 10-mm ID. Reducing the Ar/H_2 flowrate to 40 ccm/ 2.5 ccm resulted in very poor penetration and very little heat upon exposure to air.

An attempt was made to force the iron pentacarbonyl-based vapor through the sample by wrapping Teflon tape around the cylindrical sample to fit it snugly into the tube. A 50% increase in the gas pressure was required to force the vapor through the sample. The sample was more evenly covered, but still had a visible gradient. Upon exposure to air, this sample reached a temperature of 42 °C on its surface.

XRD patterns of the iron-deposited silica aerogels made from iron pentacarbonyl precursor showed very broad, weak peaks due to magnetite and possibly iron (Fig. 6). Although the pattern is noisy, the estimated peakwidth indicates that the magnetite crystallites are less than 10 nm in size.

Deposition on Carbon Aerogels

Aerojet carbon aerogels that were coated with iron from iron pentacarbonyl, under conditions similar to those used to coat silica, showed a wide range in thermal output upon exposure to air. Some samples reached temperatures of ~100 °C, while others got hot enough to ignite the substrate and combust. Attempts to produce additional metallic iron by post-treatment at 400 °C in flowing Ar/ H_2 had no effect. The black color of the carbon aerogel substrates made it impossible to visually determine the extent of penetration of the iron pentacarbonyl. XRD patterns of uncombusted samples showed broad

peaks for both magnetite and iron metal. The magnetite crystallite size was ~11 nm, similar to the crystallite size of iron phases deposited on silica aerogel.

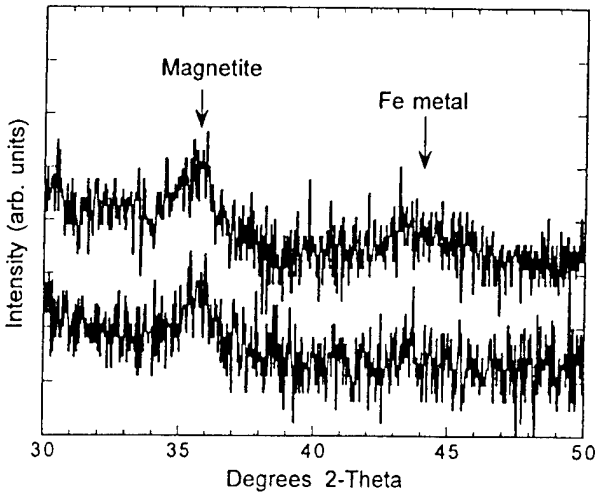

Fig. 6. XRD patterns of iron pentacarbonyl deposited on carbon (top) and silica (bottom) aerogels.

Ocellus carbon aerogels coated with iron from iron pentacarbonyl always ignited and burned, at least partially, upon exposure to air. The samples burn from the outer surfaces inward, therefore the burn duration depends on the sample size. A ~0.15-cm^3 sample burned for roughly 3 min. Figure 7 shows the radiant intensity as a function of time in the SW, MW, and SW regions. The MW:LW ration at the peak intensity corresponds to an equivalent peak blackbody temperature of ~700 °C.

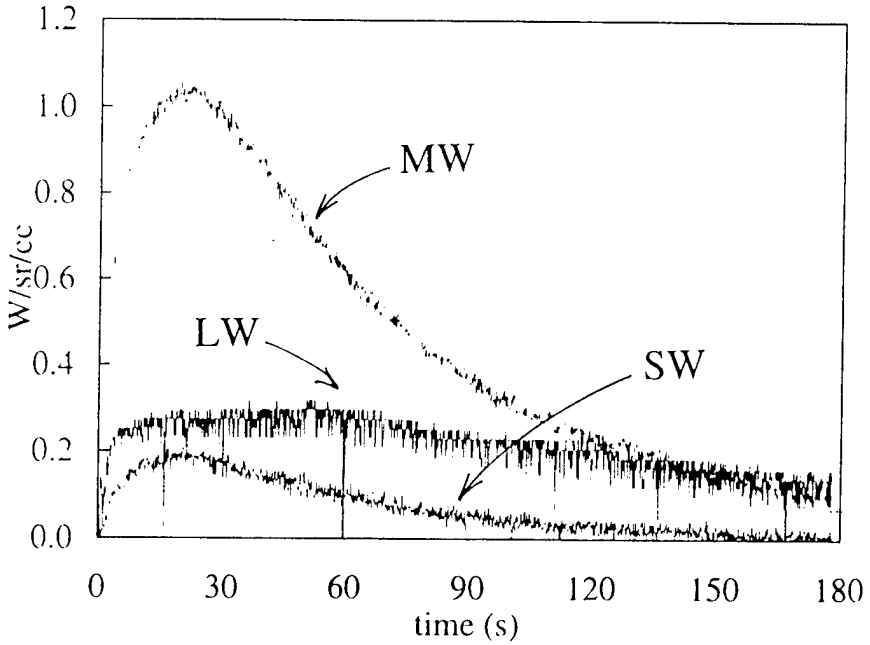

Fig. 7. Radiant intensity on a volume basis at LW, MW, and SW as a function of time of iron-coated carbon aerogel upon exposure to air.

Deposition on Resorcinol/Formaldehyde Aerogels.

Deposition of iron from iron pentacarbonyl on both Aerojet and Ocellus RF aerogels also resulted in samples that ignited upon exposure to air. As for the coated Ocellus carbon samples, the iron-RF samples glowed orange-red and burned slowly, starting at the outer surface. A ~0.700-cm^3 substrate burned for over 7 min. The small residue that remained after burning was primarily hematite (Fe_2O_3) (Fig. 8).

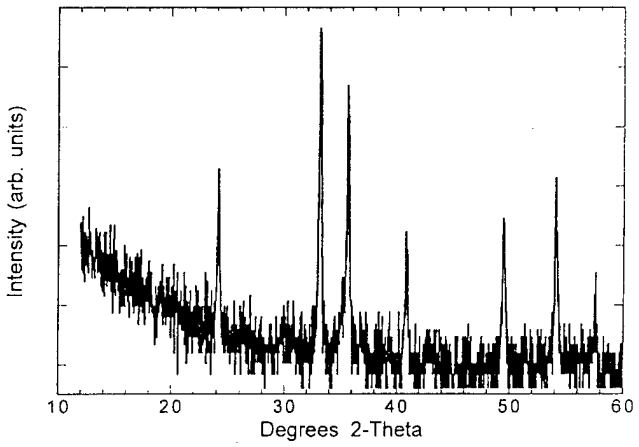

Fig. 8. XRD pattern of residue after burning an Aerojet RF aerogel deposited with iron from iron pentacarbonyl. The peaks match those for hematite (Fe_2O_3)

The volatile species generated by burning the coated RF aerogel in air have been determined by mass spectrometry. The most abundant by-products are benzene and toluene, followed by ethyl benzene or para-xylene, and ortho-xylene. Minor amounts of trimethylbenzene are also produced. Table 2 shows the amount of each detected species measured during a partial burn of a sample. Because the sample did not burn completely during the measurement, the amount of volatile species released on a mass or volume basis is not precisely known.

Figure 9 shows the IR radiant intensity measured for an iron-deposited Ocellus RF aerogel upon exposure to air. Based on the MW:LW ratio at the peak intensity, the sample is estimated to have produced an equivalent peak blackbody temperature of 600 °C.

DISCUSSION

The Fe-Si oxide aerogels prepared by the sol-gel method do not show any promise as thermally emitting materials. Based on the presence of metallic iron in the XRD patterns of samples exposed to air, much of the iron in the aerogel remains unreacted. The iron crystallite size (54 nm) may be too large to completely oxidize. In addition, the iron particles could be covered with an oxide or silicate layer, impeding oxygen diffusion to the inner iron core. Weak XRD peaks due to wustite (FeO) and fayalite (Fe_2SiO_4) are observed after reduction for 12 h, but thin layers, undetectable to XRD, could form a barrier even after shorter treatments.

Samples prepared by MOCVD of iron-based coatings on aerogel substrates produced varying amounts of heat. The silica aerogels coated with ferrocene emitted only small amounts of heat, though

these samples had the largest weight gain and therefore presumably the most material deposited. It is possible that the deposited material clogged the smaller pores, thereby preventing oxidation of much of the iron in the sample because of hindered airflow into the aerogel interior. This explanation is consistent with the decrease in BET surface area following deposition and the presence of Fe metal in the XRD pattern even after the substrates were exposed to air. Furthermore, the volatility of ferrocene, which makes it a good CVD precursor, may also be a drawback if material initially deposited is subsequently volatilized and lost during the thermal reduction process.

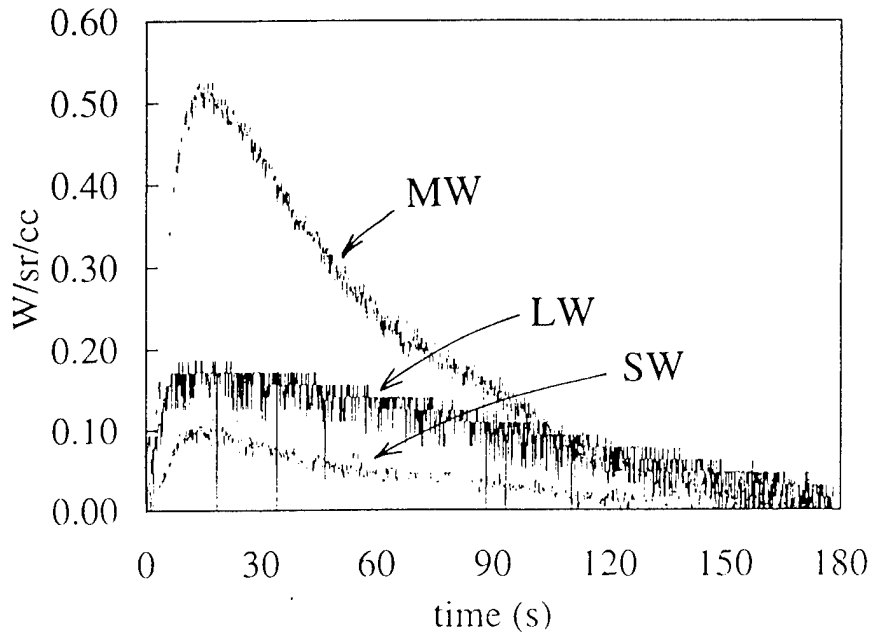

Fig. 9. Radiant intensity on a volume basis at LW, MW, and SW as a function of time of iron-coated RF aerogel upon exposure to air.

Deposition of iron from iron pentacarbonyl on silica aerogel resulted in less weight gain and little change in surface area, compared to iron deposition from ferrocene. However, the iron carbonyl-based samples reached higher temperatures upon exposure to air. Post-depositional heating in Ar/H_2 causes more complete decomposition of the carbonyl and further increases the maximum temperature observed after exposure to air. This effect was not observed in samples prepared with carbon aerogel substrates, presumably due to more complete decomposition of iron pentacarbonyl on the carbon during deposition. In spite of relatively modest thermal output, the depositions on silica aerogel were useful for visually determining the extent of penetration by the darkly colored iron compounds under various conditions.

Iron-coated RF and carbon aerogels are the most promising of the aerogels studied for thermal emitter applications. When coated with iron from iron pentacarbonyl, both the Ocellus and Aerojet RF and carbon aerogels spontaneously ignited and burned upon exposure to air. In these samples, the exothermic oxidation of the iron coating creates sufficient heat to ignite the combustible substrate. The duration of thermal emission depends on the size of the sample, with a maximum of nearly 7 minutes observed for samples approximately 0.7 cm^3 in volume. Based on MW:LW ratios at the peak radiant intensity, the RF sample produced a peak equivalent blackbody temperature of 600 °C and the carbon sample produced a peak equivalent blackbody temperature of 700 °C.

The radiant IR emission for RF and carbon aerogels deposited with iron from iron pentacarbonyl show nearly equivalent intensities in the LWIR and MWIR (Figs. 7 and 9). In all of the IR measurements

made, small samples were used in a static testing environment. A gentle stream of air over the samples increased the absolute intensity as well as the MW/LW ratio.

The range in IR output observed for the iron-coated Aerojet carbon is attributed to a combination of factors. Slight variations in the amount of iron deposited and the degree of penetration can cause a range in temperatures when exposed to air. In silica aerogels, when the iron deposited mainly on the outer surface, the local temperature at the surface was higher than when the iron penetrated more evenly. The distribution of the deposited iron in the carbon aerogels may therefore determine whether there is sufficient heat at any point in the sample to cause ignition. The Aerojet carbon samples that did not burn were made prior to obtaining the Ocellus carbon material. In experiments in which Aerojet and Ocellus materials were placed side-by-side and coated in the same run, both samples ignited when exposed to air. We believe that the samples that did not burn did not have iron deposited in adequate density (i.e. predominantly on the outer surface) to ignite the carbon.

Release of volatile organic compounds, including benzene and toluene, during combustion of the RF material makes the pyrolized carbon substrates far more attractive from an environmental and health safety standpoint. However, depending upon the specific application, RF, silica or carbon aerogel may be the most appropriate substrate material. Worst-case estimates indicate that the benzene concentration would be quickly reduced to safe levels in outdoor applications by simple diffusion.[3]

CONCLUSIONS

Iron-bearing aerogels have been developed as potential new thermally emitting materials. Efforts to prepare aerogels with nanoscale iron metal in the aerogel structure by a sol-gel route were not successful. However, MOCVD of iron on several aerogel substrates yields materials that produce varying amounts of heat upon exposure to air, depending on the substrate composition. The duration of thermal emission is up to several minutes, depending on the sample size.

Three aerogel substrate materials (silica, carbon and resorcinol/formaldehyde) and two volatile iron precursors (ferrocene and iron pentacarbonyl) were investigated. In general, samples coated with iron pentacarbonyl appear to generate more heat than equivalent samples coated with ferrocene, which fills pores, thereby blocking flow of air. In the case of RF and carbon, the heat produced by the oxidation of deposited iron was sufficient to ignite the substrate. For carbon samples, the distribution of iron may be important in determining whether the local temperature gets high enough to cause ignition. The additional heat due to the combustion of the organic substrates leads to orange-red emission in the visible and temperatures of ~600 to 700 °C for up to 7 min for ~0.7-cm samples. Volatile organic compounds, including benzene and toluene, are released during combustion of the resorcinol/formaldehyde aerogel, but are not expected upon combustion of carbon- or silica-based materials. Results to date indicate that tailoring of the chemistry, deposition parameters, and sample dimensions allows control of the thermal emission spectra and duration.

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[3] Using the semi-quantitative mass spectrometry data to make a conservative estimate, if the benzene produced by the burning of 100 cm^3 of Aerojet RF aerogel were diluted in 27 m^3 then it would be below the threshold limit allowed by OSHA.

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APPENDIX

Deposition parameters and results for iron-deposited aerogel samples

Abbreviations used in Appendix:

OC– Ocellus Carbon
ORF– Ocellus Resorcinol Formaldehyde
AC– Aerojet Carbon
ARF– Aerojet Resorcinol Formaldehyde
FT-1– Flow-through setup shown in Figure 1a
FT-2– Flow-through setup shown in Figure 1b
FT-3– Flow-through setup shown in Figure 2
SGA– Sealed glass ampoule
SSB– Sealed steel bomb
SGF– Sealed glass flask
GB-IR– Stored in glove box after deposition; IR radiance measured.

Note that reported temperatures are setpoint temperatures; sample temperature was measured to be 93 °C for a setpoint of 100 °C.

Deposition date	8/21/1996	8/29/1996	9/5/1996	9/10/1996	9/10/1996	9/18/1996	9/23/1996	9/24/1996	9/25/1996
Substrate type	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2
Substrate comments									
Precursor	ferrocene	ferrocene	ferrocene	ferrocene	ferrocene		ferrocene	ferrocene	ferrocene
Precursor set up	FT-1	FT-1	SGA	SGA	SGA		SGA	SSB	FT-1
Precursor temperature (°C)	100	100	200	150	150		150	150	110
Carrier Gas	Ar	Ar	vacuum	vacuum	vacuum	Ar/H_2	vacuum	vacuum	Ar
Flow rate (ccm)	100	100				315/35			100
Heating rate (°C/min)	5	5	5	2	2	2	2	2	5
Water removal temperature (°C)	400	400	200	150	150		150	150	400
Deposition temperature (°C)	400	400	200	150	150		150	150	400
Deposition time (hrs)	0		20	24	24		24	22	12-24
Reduction temperature (°C)						500			
Reduction time (hrs)						3			
Procedure comments	plastic line melted-no deposition	line clogged shortly after starting deposition	ampoule had a small hole	ampoule cracked			most ferrocene deposited out on cool ends of tube	aerogel covered with ferrocene	carrier tubes clogged at point during the run and had to be unclogged
Initial mass (mg)		123.7	134.2	148.5	153.4	115.9	144.6	172.8	139
Mass after deposition (mg)									
Deposition comments	entire aerogel was black	transparent throughout, no deposition	even black color	even black color	uneven, black only on the edge	even black color	even bright orange color	swirled orange and black	black rind, transparent core
Pyrophoric upon exposure to air? (Y/N)	N	N	N	N	N	N	N	N	N
Surface temperature (°C)									
Exposure comments									

Appendix: Deposition parameters and results for iron deposited aerogel samples

Deposition date	10/11/1996	10/11/1996	10/11/1996	10/11/1996	10/15/1996	10/16/1996	10/18/1996	10/21/1996	10/22/1996
Substrate type	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2
Substrate comments	heated to 500°C, held 3 hrs	heated to 500°C, held 3 hrs	heated to 500°C, held 3 hrs	heated to 500°C, held 3 hrs	heated to 500°C, held 3 hrs	heated to 500°C, held 3 hrs	heated to 500°C, held 30 min	heated to 500°C, held 30 min	heated to 500°C, held 30 min
Precursor	$Fe(CO)_5$	ferrocene	ferrocene	ferrocene			$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$
Precursor set up	SGF	SSB	SSB	SSB			FT-3	FT-3	FT-3
Precursor temperature (°C)	RT	170	170	170			RT	RT	RT
Carrier Gas		vacuum	vacuum	vacuum	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2
Flow rate (ccm)							65/3.2	65/3.2	100/5
Heating rate (°C/min)		5	5	5	5	5	5	5	5
Water removal temperature (°C)		170	170	170			250	250	180
Deposition temperature (°C)		170	170	170			150	125	125
Deposition time (hrs)		48	48	48			3	2:10	1:38
Reduction temperature (°C)	150	250	250	250	500	500			
Reduction time (hrs)	6	48	48	48	3	3			
Procedure comments							Pyrex tube and a-gel coated with silver flakes	deposition done until silver flakes started to deposit on outside of a-gel	a-gel was wrapped with Teflon to force precursor through the pores
Initial mass (mg)	36.3	713	380	130	604.9		203	253.2	201.4
Mass after deposition (mg)					210		368	286	
Deposition comments	even silver-gray color	even black color	black w/ brown swirl	black w/ brown swirl	black w/ brown swirl	even black color	black/dark brown gradient	black rind with light/dark brown gradient	black gradient
Pyrophoric upon exposure to air? (Y/N)	Y	N	N	N	N	Y	Y	Y	Y
Surface temperature (°C)	very low					very low	melted plastic	lots of heat	42
Exposure comments	turned yellow after exposure to air						silver flakes turned black/blue after exposure		unwrapping Teflon caused a-gel to break into several pieces

Deposition date	10/23/96	10/25/1996	10/25/1996	10/28/1996	10/29/1996	10/30/1996	10/31/1936	11/1/1996	11/4/1996	11/6/96
Substrate type	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2
Substrate comments	heated to 500°C, held 30 min	4:2 - buffer:TMOS heated to 500°C, held	4:2 - buffer:TMOS heated to 500°C, held	3:2 - buffer:TMOS heated to 500°C, held	3:2 - buffer:TMOS heated to 500°C, held	4:2 - buffer:TMOS heated to 500°C, held	3:2 - buffer:TMOS heated to 500°C, held	3:2 - buffer:TMOS heated to 500°C, held	3:2 - buffer:TMOS heated to 500°C, held	3:2 - buffer:TMOS heated to
Precursor	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	ferrocene	$Fe(CO)_5$	ferrocene	ferrocene	$Fe(CO)_5$	ferrocene
Precursor set up	FT-3	FT-3	FT-3	FT-3	FT-2	FT-3	FT-2	FT-2	FT-3	FT-2
Precursor temperature (°C)	RT	RT	RT	RT	>100	RT	>100	>100	RT	>100
Carrier Gas	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar	Ar/H_2	Ar	Ar	Ar/H_2	Ar
Flow rate (ccm)	65/3.2	65/3.2	65/3.2	65/3.2	65	65/3.2	65	65	65/3.2	65
Heating rate (°C/min)	5	5	5	5	5	5	5	5	5	5
Water removal temperature (°C)	250	250	250	250	400	250	400	400	250	400
Deposition temperature (°C)	110	100	100	100	400	100	400	400	100	400
Deposition time (hrs)	3	3	3	5	2	3	2	2	3	2.5
Reduction temperature (°C)									400	
Reduction time (hrs)									1	
Procedure comments	GB-IR	no silver flakes deposited on a-gel, GB-IR	no silver flakes deposited on a-gel	left in flowing Ar/H_2 overnight, GB-IR		GB-IR	GB-IR			
Initial mass (mg)	321.5	264.8	293.7	640.3	303.4	262.5	314.8	313.6	395.3	574.8
Mass after deposition (mg)	364									
Deposition comments	black rind, transparent inside	black/brown gradient	black/brown gradient	even black color	even black color	black/silver gradient	even black color	even black color	black/gray gradient	even black color
Pyrophoric upon exposure to air? (Y/N)	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Surface temperature (°C)			>48				very little	very little	72	36
Exposure comments			above 30 for 7 min						stayed above body temp for 1:20	slow to reach temperatu re

Deposition date	11/12/1996	11/13/1996	11/15/1996	11/18/1996	11/18/1996	11/18/1996	11/19/1996	11/19/1996	11/19/1996
Substrate type	AC	AC	SiO_2	ARF	ARF	ARF	ARF	ARF	ARF
Substrate comments									
Precursor	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$
Precursor set up	FT-3	FT-3	FT-3	FT-3	FT-3	FT-3	FT-3	FT-3	FT-3
Precursor temperature (°C)	RT	RT	RT	RT	RT	RT	RT	RT	RT
Carrier Gas	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2
Flow rate (ccm)	65/3.2	65/3.2	65/3.2	65/3.2	65/3.2	65/3.2	65/3.2	65/3.2	65/3.2
Heating rate (°C/min)	5	5	5	5	5	5	5	5	5
Water removal temperature (°C)	250	250	250	250	250	250	250	250	250
Deposition temperature (°C)	100	100	100	100	100	100	100	100	100
Deposition time (hrs)	3	3	3	3	3	3	1	1	1
Reduction temperature (°C)		400							
Reduction time (hrs)		1							
Procedure comments						GB-IR			
Initial mass (mg)	331	566.8	412.6	81.5	99.5	118.5	136	204.5	310.3
Mass after deposition (mg)									
Deposition comments	even black color	black color	black/transparent gradient	black color	black color	black color	black color	black color	black color
Pyrophoric upon exposure to air? (Y/N)	Y	Y	Y	Y	Y	Y	Y	Y	Y
Surface temperature (°C)	>99	73	32	201			very little	very little	very little
Exposure comments				glowed for 4-5 min. A-gel burned away leaving iron	glowed for 4-5 min. A-gel burned away leaving iron	glowed for 4-5 min. A-gel burned away leaving iron			

Deposition date	11/20/1996	11/25/1996	11/25/1996	11/25/1996	11/26/1996	11/26/1996	11/26/1996	11/26/1996	12/9/1996
Substrate type	SiO_2	ARF	ARF	ARF	ARF	ARF	ARF	ARF	ARF
Substrate comments	4:2 - buffer:TMOS								
Precursor	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$
Precursor set up	FT-3	FT-3	FT-3	FT-3	FT-3	FT-3	FT-3	FT-3	FT-3
Precursor temperature (°C)	RT	RT	RT	RT	RT	RT	RT	RT	RT
Carrier Gas	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2
Flow rate (ccm)	65/3.2	65/3.2	65/3.2	65/3.2	65/3.2	65/3.2	65/3.2	65/3.2	65/3.2
Heating rate (°C/min)	5	5	5	5	5	5	5	5	5
Water removal temperature (°C)	250	250	250	250	250	250	250	250	250
Deposition temperature (°C)	100	100	100	100	100	100	100	100	100
Deposition time (hrs)	3	2	3	3	3	3	3	3	3
Reduction temperature (°C)	400								
Reduction time (hrs)	1								
Procedure comments		possible leakage of seals on valves due to glass sliver between seal and tube	possible leakage of seals on valves due to glass sliver between seal and tube	possible leakage of seals on valves due to glass sliver between seal and tube	possible leakage of seals on valves due to glass sliver between seal and tube	possible leakage of seals on valves due to glass sliver between seal and tube	possible leakage of seals on valves due to glass sliver between seal and tube	possible leakage of seals on valves due to glass sliver between seal and tube	
Initial mass (mg)	407.8	251.8	240.6	295.9	187.4	210.1	210.4	349	1663.2
Mass after deposition (mg)			222	262.7	167.3	168	193		150.5
Deposition comments	black/transparent gradient	black color	black color	black color	black color	black color	black color	black color	black color
Pyrophoric upon exposure to air? (Y/N)	N	Y	Y	Y	Y	Y	Y	Y	Y
Surface temperature (°C)		very hot	>body temp	>body temp	>body temp	>body temp	303	very hot	250
Exposure comments		glowed for 7 min, leaving reddish flakes					glowed for 6 min, leaving reddish flakes	glowed for 7 min, leaving reddish flakes	glowed for 7 min, leaving reddish flakes

Deposition date	12/9/1996	12/9/1996	12/10/1996	12/10/1996	12/10/1996	12/17/1996	12/17/1996	12/17/1996	12/18/1996
Substrate type	ARF	ARF	AC	AC	AC	ARF	ARF	ARF	AC
Substrate comments									
Precursor	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$
Precursor set up	FT-3	FT-3	FT-3	FT-3	FT-3	FT-3	FT-3	FT-3	FT-3
Precursor temperature (°C)	RT	RT	RT	RT	RT	RT	RT	RT	RT
Carrier Gas	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2
Flow rate (ccm)	65/3.2	65/3.2	65/3.2	65/3.2	65/3.2	65/3.2	65/3.2	65/3.2	65/3.2
Heating rate (°C/min)	5	5	5	5	5	5	5	5	5
Water removal temperature (°C)	250	250	250	250	250	250	250	250	250
Deposition temperature (°C)	100	100	100	100	100	100	100	100	100
Deposition time (hrs)	3	3	3	3	3	3	3	3	3
Reduction temperature (°C)			400	400	400				400
Reduction time (hrs)			1	1	1				1
Procedure comments	used for gc/ms of volitiles			never exposed to air	never exposed to air	never exposed to air	never exposed to air		Ar regulator malfunctioned, low Ar
Initial mass (mg)	185	162.6	175.3	199.5	239.9	308.5	441.9	158.1	161.1
Mass after deposition (mg)								165.5	165.8
Deposition comments	black color	black color	black color	black color	black color	black color	black color	black color	black color
Pyrophoric upon exposure to air? (Y/N)	Y	Y	Y					Y	Y
Surface temperature (°C)	very hot		hot					very hot	hot
Exposure comments	glowed for 2-3 min, leaving reddish flakes	broke into 2 small pieces before exposure	duration ~1 min					glowed for >7 min, leaving reddish flakes	lasted >1 min

Deposition date	12/18/1996	12/18/1996	1/25/1999	1/25/1999	1/25/1999	1/25/1999	2/4/1999	2/4/1999	2/4/1999	2/4/1999
Substrate type	AC	AC	ORF	ORF	ORF	ARF	ORF	OC	ORF	ARF
Substrate comments			300mg/cc	500mg/cc	700mg/cc		250mg/cc		300mg/cc	
Precursor	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$
Precursor set up	FT-3	FT-3	FT-3	FT-3	FT-3	FT-3	FT-3	FT-3	FT-3	FT-3
Precursor temperature (°C)	RT	RT	RT	RT	RT	RT	RT	RT	RT	RT
Carrier Gas	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2
Flow rate (ccm)	65/3.2	65/3.2	see below	see below	see below	see below	65/3.2	65/3.2	65/3.2	65/3.2
Heating rate (°C/min)	5	5	5	5	5	5	5	5	5	5
Water removal temperature (°C)	250	250	250	250	250	250	250	250	250	250
Deposition temperature (°C)	100	100	100	100	100	100	100	100	100	100
Deposition time (hrs)	3	3	4	4	4	4	4	4	4	4
Reduction temperature (°C)	400	400								
Reduction time (hrs)	1	1								
Procedure comments	Ar regulator malfunctioned, low Ar, never exposed to air	Ar regulator malfunctioned, low Ar, never exposed to air	600ccm flow eventually required to carry gas through setup. May be leak in connections or clog in bubbler. 400ccm required to carry gas through when bubbler was bypassed.							
Initial mass (mg)	153.8	282.7	65	90	140	42	50	75	33	32
Mass after deposition (mg)	162.3	314.1	57.4	107.1	133.5	59.9	48.4	110.1	43.2	55.7
Deposition comments	black color	black color								
Pyrophoric upon exposure to air? (Y/N)			N	Y	Y	Y	Y	Y	Y	Y
Surface temperature (°C)			26	40	32	>200				
Exposure comments						incinerated, lasted 3 min	incinerated, 2.5 min warm glow	incinerated, 3.5 min warm glow	incinerated, 1 min warm glow	incinerated (flames early), 2.5 min warm glow

Deposition date	2/8/1999	2/8/1999	2/8/1999	2/8/1999	2/25/1999	2/25/1999	3/2/1999	3/2/1999	3/16/1999	3/16/1999	3/16/1999
Substrate type	OC	ORF	ORF	OC	OC	OC	ORF	ORF	OC	OC	OC
Substrate comments		250mg/cc									
Precursor	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$
Precursor set up	FT-3	FT-3	FT-3	FT-3	FT-3	FT-3	FT-3	FT-3	FT-3	FT-3	FT-3
Precursor temperature (°C)	RT	RT	RT	RT	RT	RT	RT	RT	RT	RT	RT
Carrier Gas	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2
Flow rate (ccm)	65/3.2	65/3.2	65/3.2	65/3.2	65/3.2	65/3.2	65/3.2	65/3.2	65/3.2	65/3.2	65/3.2
Heating rate (°C/min)	5	5	5	5	5	5	5	5	5	5	5
Water removal temperature (°C)	250	250	250	250	250	250	250	250	250	250	250
Deposition temperature (°C)	100	100	100	100	100	100	100	100	100	100	100
Deposition time (hrs)	5	5	5	5	5	5	5	5	5	5	5
Reduction temperature (°C)											
Reduction time (hrs)											
Procedure comments					samples were exposed to low concentration of oxygen inside glove box. A gels did not react pyrophorically at time of exposure.				GB-IR	GB-IR	GB-IR
Initial mass (mg)	43	67	34	50					52	32	44
Mass after deposition (mg)	109	87.1	46.2	105.8					63.1	42.4	67.1
Deposition comments							black color	little color change			
Pyrophoric upon exposure to air? (Y/N)	Y	Y	Y	Y	N	N	Y	N	Y	Y	Y
Surface temperature (°C)							>200				
Exposure comments	slowly ignited, 3 min warm glow	incinerated, 1.75 min warm glow	incinerated, 1.5 min warm glow	incinerated, 2 min warm glow	perhaps a slow reaction took place inside glove box		incinerated, 3 min warm glow		incinerated, 4 min slow burn	incinerated, 3 min slow burn	incinerated, 3.5 min slow burn

Appendix: Deposition parameters and results for iron deposited aerogel samples

Deposition date	3/16/1999	3/18/1999	3/18/1999	3/18/1999	3/18/1999	5/27/1999	5/27/1999	5/27/1999	5/27/1999	5/27/1999
Substrate type	OC	OC	OC	OC	OC	AC	OC	AC	OC	AC
Substrate comments						pyrolized 300mg/cc sample		pyrolized 300mg/cc sample		pyrolized 300mg/cc sample
Precursor	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$	$Fe(CO)_5$
Precursor set up	FT-3	FT-3	FT-3	FT-3	FT-3	FT-3	FT-3	FT-3	FT-3	FT-3
Precursor temperature (°C)	RT	RT	RT	RT	RT	RT	RT	RT	RT	RT
Carrier Gas	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2	Ar/H_2
Flow rate (ccm)	65/3.2	65/3.2	65/3.2	65/3.2	65/3.2	65/3.2	65/3.2	65/3.2	65/3.2	65/3.2
Heating rate (°C/min)	5	5	5	5	5	5	5	5	5	5
Water removal temperature (°C)	250	250	250	250	250	250	250	250	250	250
Deposition temperature (°C)	100	100	100	100	100	100	100	100	100	100
Deposition time (hrs)	5	5	5	5	5	4	4	4	4	4
Reduction temperature (°C)										
Reduction time (hrs)										
Procedure comments	GB-IR	GB-IR	GB-IR	GB-IR	GB-IR	beginning temperature 145°C	beginning temperature 145°C	beginning temperature 145°C	beginning temperature 145°C	beginning temperature 145°C
Initial mass (mg)	45	69	56	66	65	40	48	36	38	11
Mass after deposition (mg)	63.4	103	86.4	95.4	90.6	52	71	55	57	19
Deposition comments										
Pyrophoric upon exposure to air? (Y/N)	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Surface temperature (°C)						150	175	140	190	120
Exposure comments	incinerated, 3 min slow burn	incinerated, 3 min slow burn	incinerated, 3 min slow burn	incinerated ~2 min burn, crunched up and burned quickly	incinerated, 2.5 min slow burn, blown on to increase intensity	very slow smoldering burn, 3.5 min	sparked and popped, 4 min	sparked and popped, 3.5 min	sparked and popped, 3.5 min	sparked and popped, 2.5 min